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THE OHIO STATE UNIVERSITY
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Investigation of PHOTOEMISSIVE SURFACES

Subject of Report Progress Report for Period
July 1 to October 1, 1952

Submitted by E. N. Lassette
Department of Chemistry

Date..... July 28, 1953

PHOTOEMISSIVE SURFACES

During the period July 1 to October 1, 1952 considerable progress was made toward understanding the chemistry of the formation of the S-1 photo surface. This progress has been possible because there were no changes in the personnel during the quarter. The crystal structure of Cs_2O has also been further refined.

1. TUBE FABRICATION AT 150°C.

In the preparation of the S-1 photosurface the cesium addition is usually performed with the tube at 190° to 200°C. At these temperatures the solid cesium oxides which may be formed are CsO_2 , Cs_2O_3 , and Cs_2O . However, at temperatures below 170°C the solid cesium oxide, Cs_3O , may also be formed during the reaction of cesium with silver oxide. It has been reported⁽¹⁾ that tubes prepared by cesium addition at 150°C

(1) N.S. Zaitsev and N.S. Klebnihov, J. Tech. Phys. (USSR) 8 1023-33 (1938)

do not develop appreciable infrared sensitivity. From an investigation of the relation of photoelectric properties, composition, and cesium vapor pressure, Sayama⁽²⁾ concluded that for cathodes prepared at 145°C

(2) Y. Sayama, J. Phys. Soc. Japan 1 13-17 (1946)

the spectral sensitivity does not vary in the composition range

$2.0 < \text{Cs}/\text{O} < 3.0$, and thus that the cesium in excess of Cs_2O was present predominantly as the suboxide Cs_3O . In addition the absolute yield of photoelectric and thermionic emission remains at nearly the same values for the above range of composition. Consequently to establish the facts, an investigation has been made of the development of thermionic and photoelectric emission at 150°C using the techniques described in the previous report for fabrication at 190°C .

1.1 Experimental Methods.

A series of four massive cathode tubes have been prepared at 150°C using the same cathode and capillary in each run. Two of the tubes were used to investigate the characteristics of the thermionic and photoelectric emission during continuous addition of cesium to the formation of a conducting film on the tube wall between the cathode and anode. The second pair of tubes was used to study the effect of cooling the cesium source, cooling the tube, baking, and reintroducing cesium on the photoelectric and thermionic emission.

The massive cathode tubes used in the investigation were similar in design to those used in the 190°C investigation previously reported. The massive silver cathodes with an area of approximately 22 cm^2 were oxidized in an oxygen glow discharge to the second-order yellow color. At the second-order yellow color the oxide film contained approximately 4.5×10^{-7} gram atom of oxygen per square centimeter. At 150°C the capillary used to control the cesium flow into the tube gave 6.13×10^{-8} mole of Cs per minute (7 cathode monolayers per minute) and at room temperature 9.4×10^{-10} mole per hour.

After the oxidation and firing of the Cs_2CrO_4 -Si pellet in the side tube, the tube was tipped off the vacuum system, placed in the oven at 150°C , and connected to the vibrating reed amplifier-Brown recorder unit. During the cesium addition the thermionic emission was continuously recorded. The photoemission was periodically measured by illuminating the cathode with white light passed through the following filters:

- F_1 - Clear glass
- F_2 - Polaroid XRX-60 $> 775 \text{ m}\mu$
- F_3 - Polaroid XRM-30 $> 830 \text{ m}\mu$
- F_4 - Corning 2540 $> 800 \text{ m}\mu$
- F_5 - Polaroid XAN-14 $> 880 \text{ m}\mu$

During the tube preparation the cesium addition was stopped by the simple expedient of placing a piece of moist cotton on the cesium source to reduce the cesium vapor pressure to a negligible value for the experimental periods involved.

In the discussion of results which follows, composition data for the tubes are presented. It is worth while to comment at this point on the precision of these values. The reported cesium-flow rate into the tube is dependent upon the validity of two assumptions, namely (1) that the partial pressure of cesium in the tube is negligible compared to the cesium pressure in the source, and (2) that the cesium flow rate through the capillary may be computed using the intermediate pressure flow equation.

The experiments of Sayama (2) show that for the composition range $0.0 < \text{Cs/O} < 2.4$ the cesium vapor pressure at 145°C is less than 10^{-6} mm Hg

during cesium addition at flow rates approximately 10 times larger than used in the tube fabrication at 150°C described in this report. In addition, the equilibrium cesium vapor pressure in the tube after sealing the cesium source off at a Cs/O ratio less than 2.92 was less than 7.0×10^{-8} mm Hg. In Sayama's experiments it was observed that beyond the composition Cs/O = 2.4 the ion gauge characteristics during the cesium addition did not correspond to pure cesium and consequently the actual cesium vapor pressure could not be determined. Thus to the composition Cs_{2.4}O the cesium partial pressure in the tube should be negligible compared to the pressure in the source. In addition, it is also evident that to the gross composition Cs_{2.4}O it would be difficult to distill cesium out of the tube by cooling the cesium source.

In the case of the second assumption it has been experimentally established in this laboratory that the cesium flow rate for the capillary size used is actually 5% high if calculated by means of Knudsen's molecular flow equation. If the intermediate pressure region flow equation is used with a cesium viscosity of 49.2×10^{-5} poise at 150°C and the mean free path of cesium in cesium then the calculated and observed flows differ only by 0.9%. Thus the calculated cesium flow rate should be reliable to at least 1%.

In the calculation of the Cs/O ratios for the tubes the amount of oxygen deposited during the glow discharge is used. The magnitude of error in the oxygen content of the cathode is probably of the order of 5%. Thus the absolute value of the Cs/O ratio may be in error by 5%.

In considering the Cs/O ratios it is to be noted that these values represent the gross composition of the tubes. These values do not necessarily represent the actual composition existing at the photosurface because of the reaction of cesium with tube walls etc.

1.2 Discussion of Results

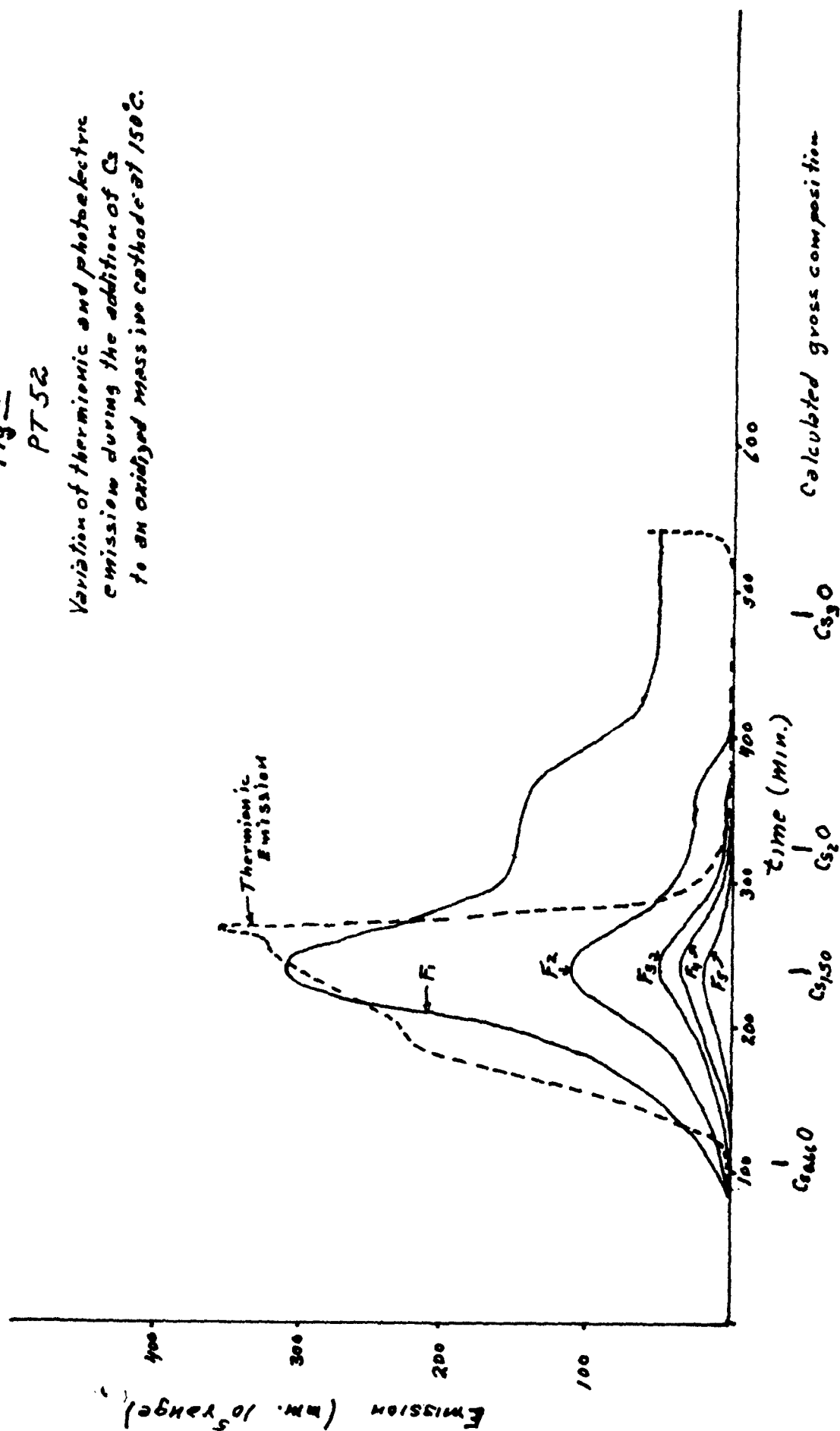
The investigation of tube fabrication at 150°C has demonstrated that for cathodes oxidized to the second-order yellow color reproducible results are obtained. Therefore, the discussion will be restricted primarily to the characteristics of two tubes, PT 52 and PT 53.

1.21 Development of thermionic and photoelectric emission on continuous addition of cesium.

In the preparation of PT 52 the cesium was added continuously until a surface conduction film was formed on the tube wall. The variation of the thermionic and photoelectric emission during continuous cesium addition to PT 52 is shown in Fig. 1. The maximum photoemission was obtained when the gross Cs/O ratio was 1.5. The thermionic emission maximum which appears at 1.6 Cs/O is actually less sharp than is indicated by the figure. This arises for the following reason: during the illumination of the cathode in the composition range 1.5 ± 0.2 , there was a marked photoactivation of the thermionic emission which resulted in a higher value for the thermionic emission than would appear if there had been no illumination. At 150°C the rate of decay to the normal value appears to be slower than at 190°C. The sharp peak in the thermionic emission curve was thus produced by the photoactivation. The maximum emission at 150°C occurs at approximately the same gross composition at 150°C as in earlier runs at 190°C.

Fig 1
PT 52

Variation of thermionic and photoelectric emission during the addition of Cs to an oxidized massive cathode at 150°C.



From the appearance of the photoemission curves it would appear that three different types of photosurfaces may be formed during the cesium addition. At the composition $\text{Cs}/\text{O} = 1.5$ the surface of maximum infrared sensitivity appears. As the cesium addition is continued the photoemission decreases to a new steady state at $2.0 \text{ Cs}/\text{O}$ as shown in Fig. 1 300 to 375 minutes. This surface has a long wavelength limit of approximately $890 \text{ m}\mu$ as indicated by the filter responses. During this process the thermionic emission decreased to the order of 10 mm (10^5 range) compared to 330 mm (10^5 range) at the maximum. Further addition of cesium resulted in a second decrease in photoemission at 375 to 400 minutes to a surface with a long wavelength limit less than $800 \text{ m}\mu$. For this surface the thermionic emission had decreased to 0.17 mm (10^5 range).

Shortly before the composition Cs_3O is reached the emission starts to change from a thermionic current to a conduction current. This is indicated by the fact that the current becomes directly proportional to the applied voltage and the reverse polarity current equals the correct polarity current. At the composition $3.2 \text{ Cs}/\text{O}$ the reverse polarity is equal to the correct polarity and the equivalent resistance is $1.4 \times 10^{10} \Omega$. It is of interest to note that this leakage current probably is not due to pure metallic cesium since cooling a tube which has a conduction film at 150°C results in a decrease in conductivity. Measurements on the conductivity of these films as a function of temperature has indicated that the film has a conductivity work function of approximately 0.3 ev .

The appearance of the conduction current is related to the gross composition of the tube. At 190°C the equilibrium phase for $2.0 < \text{Cs/O} < 2.91$ is a solution of oxygen in cesium liquid in equilibrium with Cs_2O . At 150°C, however, for $2.0 < \text{Cs/O} < 3.0$ the equilibrium phases are solid Cs_2O and solid Cs_3O , but for $3.0 < \text{Cs/O} < 3.29$ the equilibrium is between cesium liquid and solid Cs_3O . Experimentally it is observed that the conduction current appears at approximately 2.1 Cs/O for 190°C and at approximately 3.0 Cs/O for 150°C tubes. The fact that the conduction current appears at a gross composition involving the presence of liquid cesium in the tube suggests that to a first approximation the composition within the tube corresponds to chemical phase equilibria. Thus between the composition Cs_2O and Cs_3O the species Cs_3O undoubtedly is formed.

The results described above show how thermionic emission and photosensitivity develop as cesium is added to the photocathode without interruption. The results show that both thermionic and photoelectric emission are considerably reduced after passing the composition $\text{Cs/O} = 2$ and hence suggest, at first sight, that Cs_3O which is formed beyond this composition is not active in the far infrared. It is of interest, however, to pursue the matter further by adding cesium beyond the composition $\text{Cs/O} = 2$ and then to bake the phototube at elevated temperatures for considerable times to see whether the infrared sensitivity can be recovered. This has been done in several instances; one of which is discussed in the following section. At the same time several other experiments have been performed for different purposes. All of these are described in the next section.

1.22 Effect of cesium addition in excess
followed by heating

During the preparation of PT 53 at 150° C the effect of the following operations on the thermionic and photoelectric emission were investigated:

1. Cooling of the cesium source during cesium addition at 150°C. This interrupts the flow of cesium to the photocathode.
2. Repeated addition of cesium at 150°C, recooling of cesium source to equilibrate the tube, and then cooling the tube to room temperature.
3. Addition of cesium to the tube at room temperature followed by rebaking with the cesium source cool.

In Table I data are presented summarizing the processing conditions and the room temperature spectral response characteristics. It is of interest to note that the spectral response characteristics after bake are essentially constant for the composition range $1.615 \leq \text{Cs/O} \leq 2.82$. In Table I the first column contains the number assigned to each heat treating operation so as to identify the operation in subsequent figures. Column 2 gives the temperature to which the tube is heated. Column 3 gives the number assigned, for identification purposes, to the spectral response measurement. The spectral responses were measured at room temperature. Column 4 gives the time in hours and minutes at which the spectral response measurement was made. Column 5 gives the temperature of the side tube containing cesium during the interval preceeding the spectral response measurement. In the interval preceding measurements 2, 3, 4, 5, 6, 7, 9, 12, 13, 14, 15, 16 and 24 both the cesium source and the attached phototube were maintained at room temperature. Column 6 gives the time (in minutes) during which the cesium source was at oven temperature

TABLE I. FABRICATION DATA FOR PT 53

Bake	Temp.	Spect. response	Spect. response (hr:min)	Cs source (°)	Cs source hot(min)	Cs/o spect.	Peak λ	1/2 Max. λ	Long λ
Feb.	150	1		150	241.2	1.609	900/750	1095	1350
		2	0	30		1.609	950/750	1125	1400
		3	21:40	30		1.611	950/750	1090	1350
		4	42:05	30		1.613	900/750	1030	1250
		5	59:50	30		1.614	875/750	1000	1200
		6	64:15	30		1.615	750	950	1200
		7	85:45	30		1.617	765	950	
1	190	8	88:30	< 100		1.618	975	1120	1400
		9	108:20	30		1.619	965	1100	1400
2	190	10	109:40	190	4	1.78	930	1030	1250
3	150	11	134:35	150	42.0	2.062	985	1115	1450
		12	153:35	30		2.063	930	1040	1300
		13	157:45	30		2.064	900	1000	1200
		14	179:25	30		2.066	775	930	1125
		15	207:00	30		2.069	775	905	1100
		16	248:45	30		2.072	775	890	1100
4	150	17	251:05	< 100		2.072	985	1120	1450
5	150	18	254:10	150	12.7	2.160	985	1115	1400
6	150	19	272:30	150	18.5	2.28	980	1115	1400
7	150	20	283:07	150	41.3	2.56	970	1095	1400
8	150	21	296:17	150	39	2.82	950	1060	1350
9	150	22	300:17	150	26	3.00	900	1010	1200
10	150	23	321:17	< 100			895	990	1225
		24	389:17	30		3.001	750	870	1050

during the baking operation. This constitutes the time interval during which cesium is added to the photosurface at a high rate. During the remainder of the interval the source was cooled to 100°C in order to reduce the cesium flow rate and examine the effect on thermionic emission and photoelectric emission. Column 7 gives the ratio of atoms of cesium which have entered the phototube to the atoms of oxygen added in the initial oxidation. Columns 8, 9, 10 give respectively the wavelength in μ at the peak of the spectral response curve, at one-half the maximum and at the long wave limit. In the following discussion several significant aspects of the behavior of this tube will be pointed out.

The development of the photoelectric and thermionic emission in PT 53 during the initial cesium addition is shown in Fig. 2. During the cesium addition, the photoemission passed a maximum at 245 minutes and the cesium source was cooled. On cooling the cesium source there was a marked increase in the $(F_1 - F_2)$ photoresponse and the thermionic emission rose to a maximum. The discontinuity in the thermionic emission beyond the maximum is due to the cesium source having warmed and then being recooled. The thermionic emission characteristics of the tube are very sensitive to the addition of cesium at this stage in the fabrication. Cooling the cathode to room temperature resulted in a marked increase in the infrared response as shown by the increase in F_2 , F_3 , F_4 , and F_5 in Fig. 2.

For comparison, the following facts concerning the fabrication of photocathodes at 190°C should be kept in mind. During the fabrication

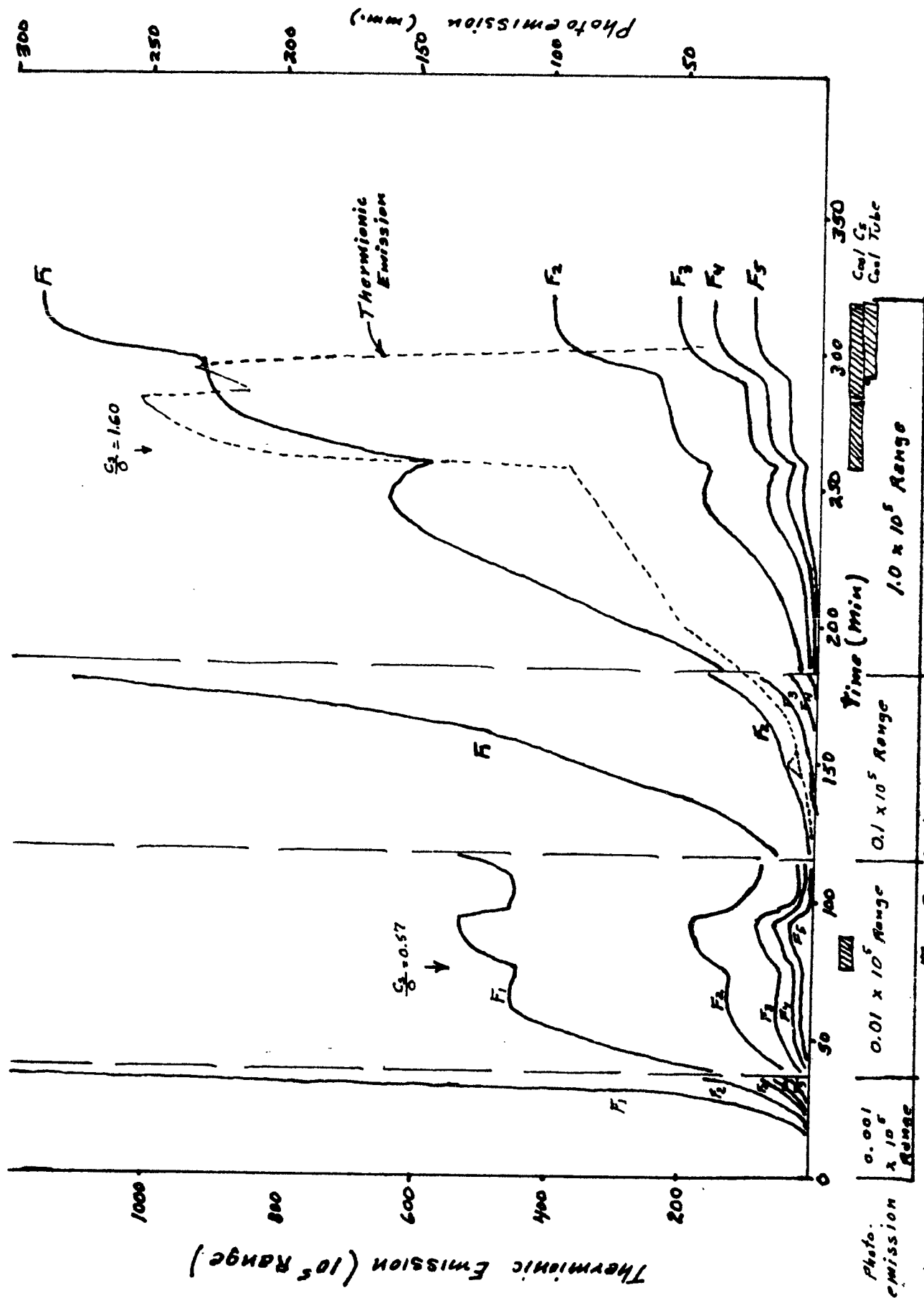


Fig. 2 Initial Cs addition to PT 53

of tubes at 190°C it is observed that cooling the cesium source may result in a decrease, an increase followed by a decrease, or an increase to a stable value for the photoelectric and thermionic emission depending upon the gross composition. These cases are encountered in the order given as more cesium is added to the phototube. As the gross composition 1.6 - 1.7 Cs/O is approached the stability of the surface formed on cooling the cesium increases and the emissions tend to stable high temperature values.

In the initial preparation of PT 53 the cesium source was cooled at 0.57 Cs/O and 1.60 Cs/O. As shown in Fig. 3, the thermionic and photoelectric emissions increased to maximum values. A comparison of the relative photoemissions for the two Cs/O ratios is shown in Table II. These data suggest that the photoelectric yield as a function of wavelength of the two surfaces 0.57 Cs/O and 1.60 Cs/O differ only by a

TABLE II. EFFECT OF COOLING CESIUM
ON THE PT 53 PHOTOEMISSION

Cs/O	Stage	F_2/F_1	F_3/F_1	F_4/F_1	F_5/F_1	White light responses (Photocurrent) F_1
0.57	Before Cs cool	0.294	0.103	0.065	0.035	1.07
	After Cs cool	0.332	0.161	0.103	0.061	1.31
1.60	Before Cs cool	0.262	0.115	0.078	0.048	159.0
	After Cs cool	0.333	0.116	0.125	0.066	180.5

scale factor despite the fact that the photocurrents differ by more than a hundred fold. This is in accord with the view that the emitting centers in the two cases are alike but are more numerous in one case than in the other.

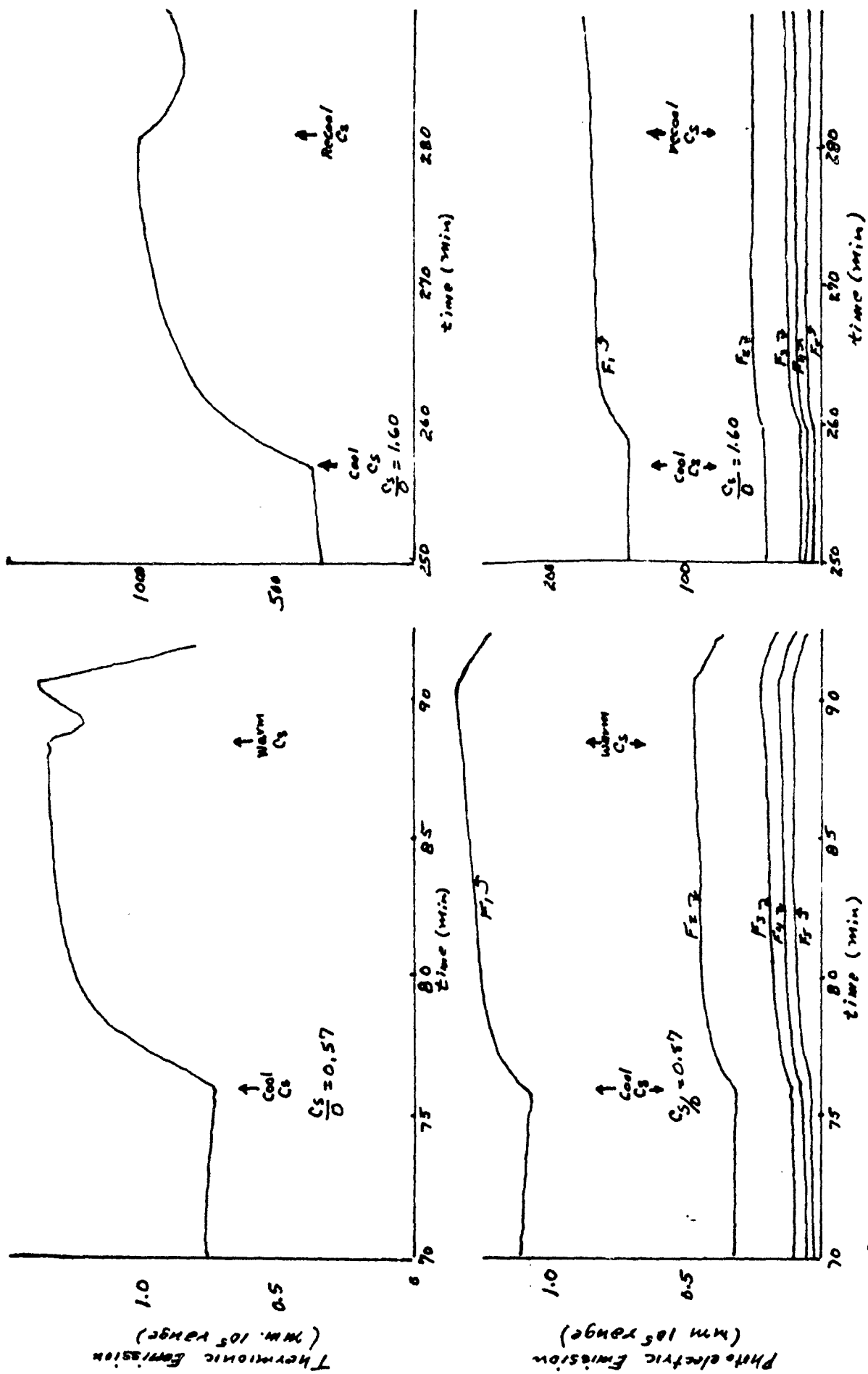


Fig. 3 Effect of cooling Cs source at $\frac{C_s}{D} = 0.57$ and 160 during fabrication of PT53 at 150°C.

In the preparation of PT 53 it was observed that, at 0.33 Cs/O, cooling the cesium source resulted in a rapid decrease in emission whereas at 0.66 Cs/O the emission increased steadily to a limiting value. It is interesting to note that the composition 0.6 Cs/O is within experimental error that corresponding to the compound Cs_2O_3 . In addition, the cesium vapor pressure data of Sayama indicate that at 145°C and low Cs/O ratios a significant partial pressure of cesium is not developed in the tube, thus the cesium reacts rapidly with the oxide film.

The above described behavior (at 150°C) of PT 53 on interrupting cesium flow (by cooling the source) differs from that encountered in the preparation of photocathodes at 190°C in one particularly important respect. Namely, in the intermediate composition range, $0.6 < \text{Cs/O} < 1.6$, at 150°C no case is encountered in which, on interrupting cesium flow, the thermionic emission first rises and then falls. This difference in behavior cannot be attributed to different rates of cesium addition at the two temperatures because the capillary size was changed so as to make the flow rates approximately equal.

The data suggest that some reaction rates involved in the formation of the photosurface become markedly slower on decreasing the reaction temperature from 190° to 150°C. However, with the present data, it is not readily possible to evolve a unique hypothesis to account for the results. It is possible that at the photosurface approximate phase equilibrium is established during fabrication at 150° and 190°C, and that the loss in emission at 190°C involves a secondary process such as reaction of cesium with the glass. Alternatively it is possible

that at 150°C a "layer" phase equilibrium $Ag_xO_y-CsO_2-Cs_2O_3-Cs_2O$ is established but that the rate of equilibration of the surface to true phase equilibrium is slow. In this case the decay in emission at 190°C could be associated with a thermal decomposition of residual silver oxide and a corresponding destruction of the photosurface by the evolved oxygen. Still another possible explanation is that at 190°C the diffusion rate of oxygen through the layer structure is rapid enough until the composition approaches 1.6 Cs/O that the infrared photosurface is unstable until the thickness is sufficient to reduce the diffusion rate to the surface to a negligible value. To establish the correct hypothesis further experiments on the stability of the high temperature surface as a function of baking time must be performed.

As mentioned earlier the spectral response characteristics (maximum photoemission wavelength, long wavelength limit, and half maximum photocurrent), remain essentially constant for the composition range $1.61 \leq Cs/O \leq 2.82$. These quantities indicate the shape of the spectral sensitivity curve. During the baking operations, depending upon the stage of fabrication, the photocurrents undergo considerable variation. The photocurrents obtained on illumination through the various filters (1) just prior to cooling the cesium source, (2) after cooling the cesium source, and (3) after cooling the tube to room temperature are presented in Table III. The photocurrent ratios are also given. In considering the data in Table III it is important to note that Bakes 1 and 2 were performed at 190°C. The data for Bake No. 2 do not necessarily represent equilibrium conditions in the tube because of experimental difficulties encountered in maintaining the cesium source cool.

TABLE III. FILTER RESPONSE DATA FOR PT 53

Stage 1 - Just before cooling cesium source

Stage 2 - After cooling cesium source

Stage 3 - After cooling tube to room temperature

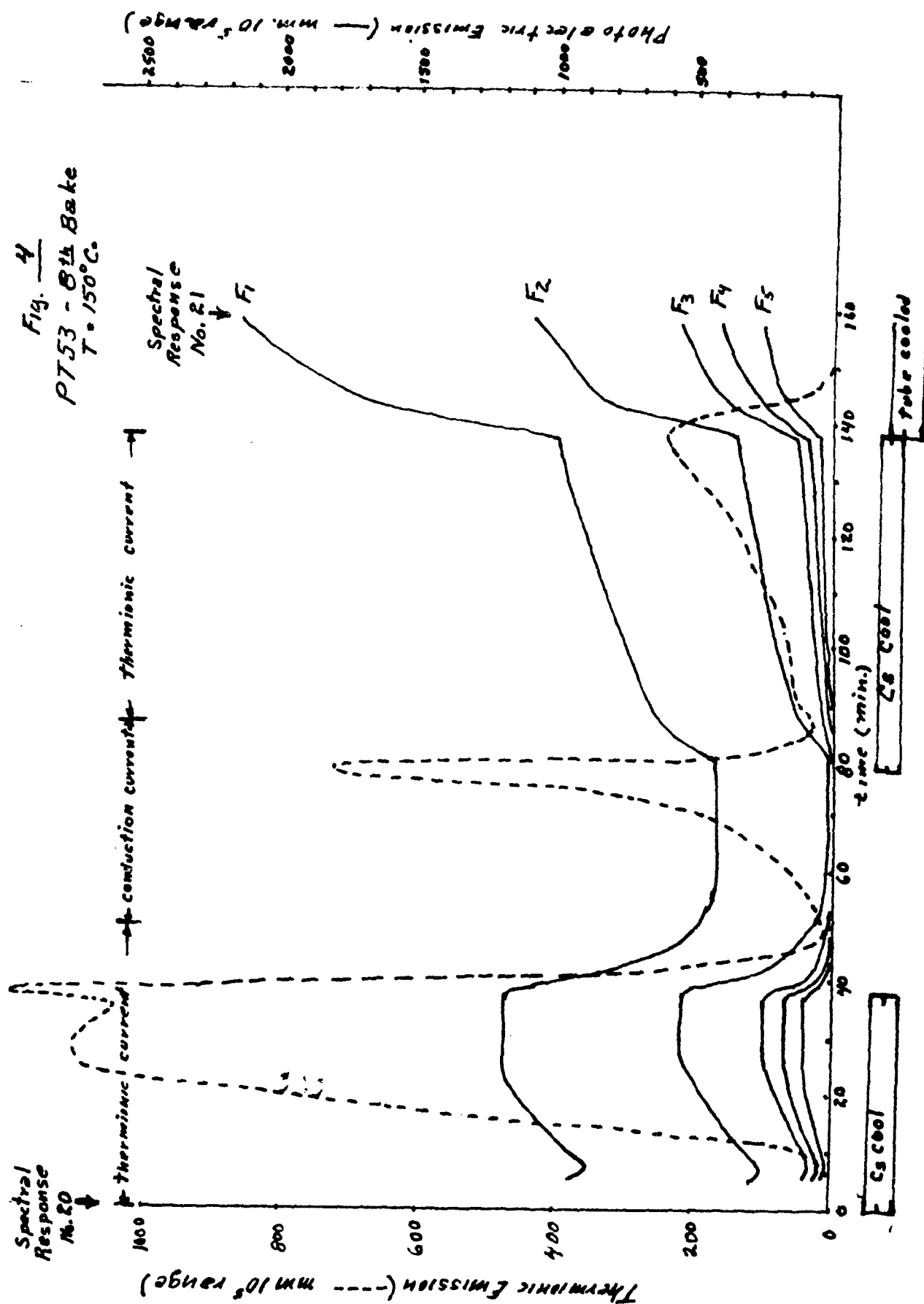
Bake No.	Stage	Filter Response(mm 10 ⁵ range)					Relative Filter Response			
		F ₁	F ₂	F ₃	F ₄	F ₅	F ₂ /F ₁	F ₃ /F ₁	F ₄ /F ₁	F ₅ /F ₁
Init.	1	159	42	18.4	12.4	7.6	0.262	0.115	0.078	0.048
	2	180	60	30	22.5	12.0	0.333	0.166	0.125	0.066
	3	290	99	54	40.4	25.2	0.341	0.186	0.139	0.087
1	1									
	2	195	55				0.282			
	3	364	150	83	60	40	0.412	0.228	0.165	0.110
2	1	830	340	150	95	50	0.410	0.181	0.126	0.060
	2	820	322	150	105	54	0.392	0.183	0.128	0.066
	3	695	230	102	68	35	0.331	0.147	0.098	0.050
3	1	560	240	110	71	40	0.429	0.196	0.127	0.071
	2	780	400	210	150	95	0.513	0.269	0.192	0.122
	3	1020	545	320	235	150	0.535	0.314	0.230	0.147
4	1									
	2	608	305	164	116	72	0.502	0.270	0.191	0.118
	3	790	435	250	195	130	0.550	0.316	0.246	0.164
5	1	380	140	52	34	15	0.368	0.137	0.089	0.039
	2	620	310	150	102	68	0.500	0.242	0.169	0.110
	3	895	472	270	202	132	0.528	0.301	0.225	0.147
6	1	386	126	42	28	12.4	0.326	0.109	0.072	0.032
	2	610	302	160	105	62	0.495	0.262	0.172	0.102
	3	930	500	295	220	145	0.538	0.317	0.236	0.156
7	1	300	70	13	7	1	0.233	0.043	0.023	0.003
	2	460	200	90	60	22	0.435	0.196	0.130	0.043
	3	800	422	240	180	115	0.526	0.300	0.225	0.144
8	1	430	15.2	1.4	1.5	--	0.035	0.003	0.003	--
	2	970	350	124	84	39	0.360	0.128	0.086	0.004
	3	2150	1080	570	410	250	0.502	0.265	0.191	0.116
9	1	375	15				0.04	--	--	
	2	554	82	12	7.5	0.5	0.148	0.022	0.014	0.009
	3	1555	605	235	155	75	0.389	0.151	0.100	0.048
10	1									
	2	710	160	35.5	21	5.5	0.225	0.050	0.030	0.008
	3	1150	470	147	95	45	0.409	0.128	0.083	0.039

The characteristics of the photoelectric and thermionic emission during the cesium addition were similar to those shown in Fig. 1 for PF 52. After the Cs/O ratio was greater than 2.0, the addition of cesium caused a decrease in the F_2 , F_3 , F_4 , and F_5 photoemission. However, cooling the cesium source resulted in an increase in the photoelectric and thermionic emission, the magnitude increasing as the Cs/O ratio increased. To the composition 2.56 Cs/O Bake 7, the thermionic emission at 150°C with the cesium source cool remained at the same order of magnitude. At the end of Bake 7 the maximum thermionic emission at 150°C with the cesium source cool had decreased to approximately half the previous value; however, the spectral response after Bake 7 did not differ significantly from the response present at the end of Bakes 3, 4, 5, and 6. As the Cs/O ratio increased it was also observed that the increase in infrared sensitivity on cooling the tube became greater so that the final surfaces from Bake 3 through 7 were practically identical in photoemission characteristics.

In the cases when the cathode was rebaked at 150°C with the cesium source cooled and no appreciable amount of cesium had been added at room temperature, the photoemission decreased reversibly to the value previously existing at the high temperature. Thus the gain and loss of photoemission with temperature is reversible in the absence of a composition change.

As shown in Table III there was a marked increase in the photoemission during Bake 8. The variation in the thermionic and photoelectric emission during this bake is shown in Fig. 4. During the initial heating with the cesium source cool there was a decrease in the photoemission followed by

Fig. 4
PT53 - 8¹⁴ Bake
T = 150°C.



an increase to "stable" values. The thermionic emission, however, increased to $\sim 1100 \text{ mm } (10^5 \text{ range})$ as compared to approximately $500 \text{ mm } (10^5 \text{ range})$ at the end of Bake 7. This high emission value is comparable to that present at the end of Bakes 3 through 6. The decrease in photoemission to a minimum observed during the heating period is attributed to the distillation of cesium from the walls to the photosurface. As the temperature increased this excess cesium reacted at the surface to form the "stable" emitter surface.

After the photoemission became constant (see Fig. 4) the cesium source was warmed to 150°C . During the cesium addition the thermionic emission decreased to a minimum and was replaced by a conduction current as shown in Fig. 4. Accompanying these changes there was a marked decrease in photoemission, the F_5 response actually disappeared, and the long wavelength limit was less than $890 \text{ m}\mu$. Recooling the cesium source resulted in the disappearance of the conduction current and the re-appearance of thermionic emission. After maintaining the cesium source cool for 60 minutes the thermionic emission had increased to $240 \text{ mm } 10^5 \text{ range}$ compared to $1100 \text{ mm } 10^5 \text{ range}$ prior to the cesium addition. During the cooling of the tube to room temperature there was a marked increase in the infrared photoemission as shown in Fig. 4.

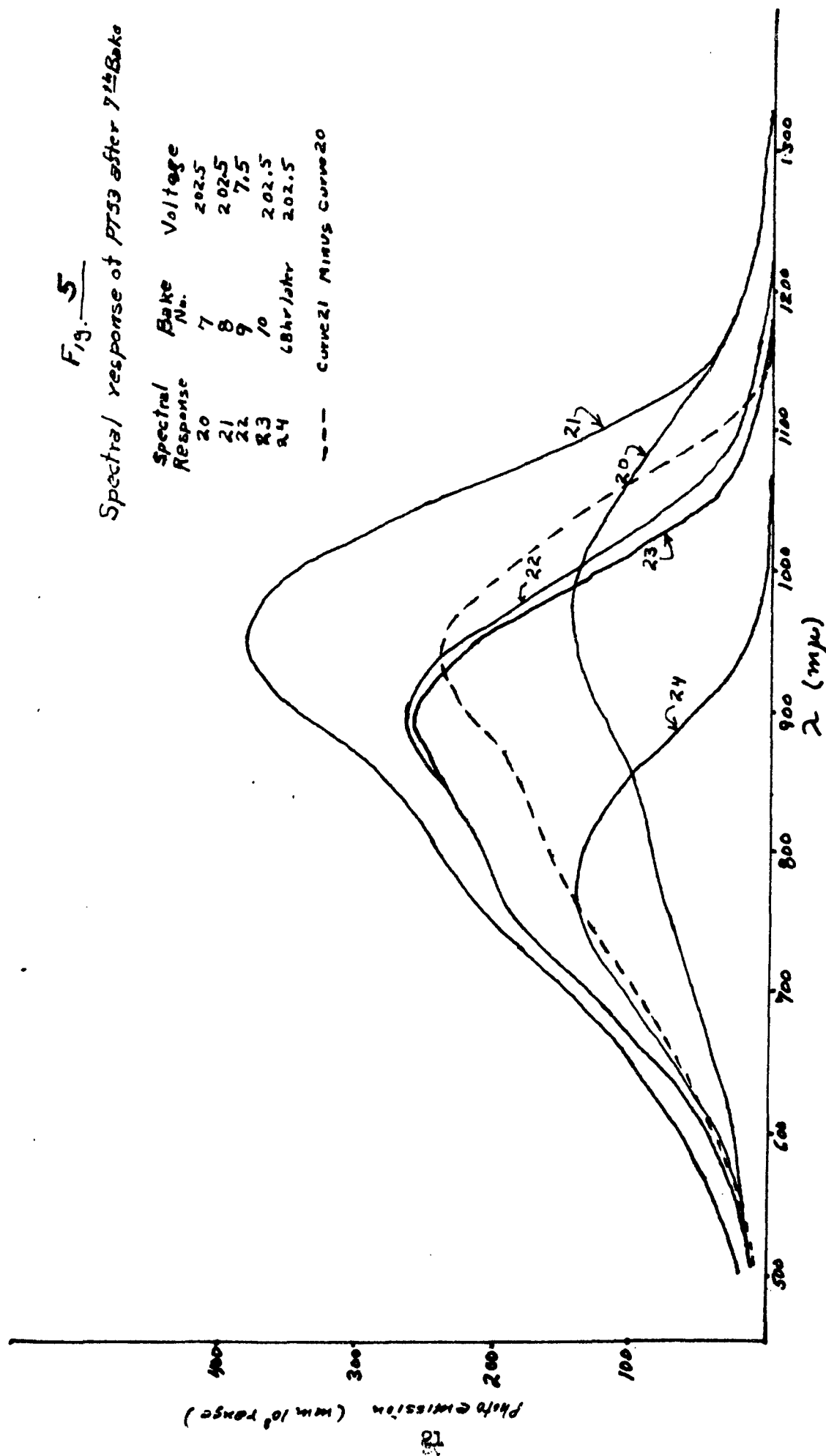
The changes in the spectral response characteristics before and after Bake 8 are shown in Fig. 5. From Bake 3 through 7 no marked changes in spectral response occurred, thus curve 20 in Fig. 5 may be considered as representative of this series. After Bake 8 the response shown in curve 21 was obtained, the marked increase in sensitivity is

Fig. 5

Spectral response of PT33 after 7th Bake

Spectral Response	Bake No.	Voltage
20	7	202.5
21	8	202.5
22	9	7.5
23	10	202.5
24	68hr/ohr	202.5

--- Curve 21 Minus Curve 20



evident. Bake 8 shifted the maximum from 970 μ to 950 μ , the long wavelength limit from 1400 to 1350, and the half-maximum photocurrent from 1095 to 1060 μ . In Fig. 5 the dotted curve represents the increase in photoemission that was obtained. Actually the difference in the long wavelength region ($\lambda > 1150 \mu$) for the two curves was small. The occurrence of the increase in photoemission with a corresponding decrease in thermionic emission is not unusual. It has been observed by Asao⁽³⁾ in the case of thin film cathodes that evaporation of a

(3) S. Asao, Proc. Phys. Math. Soc. Japan 22 448-86 (1940)

third silver layer may cause an increase in photoemission and a decrease in thermionic emission with the thermionic work function remaining constant.

During Bake 9 the tube was heated to 150°C with the cesium source cool and the thermionic emission rose gradually to the value at the end of Bake 8. During Bake 9 additional cesium was added to the tube producing a larger conduction current than in the previous bake. Baking the tube at 150°C for a short time (~ 10 min) with the cesium source cool caused a decrease in the conduction current. Cooling the tube to room temperature did reduce the leakage current to a sufficiently low value so that the spectral response could be measured using a 7.5-volt collecting field. The spectral response after Bake 9 is shown by curve 22 in Fig. 5. Further baking at 150°C with the cesium source cool reduced the conduction current and added a thermionic emission component. The spectral response at 202.5 volts after Bake 10 corresponds to curve 23

in Fig. 5. The addition of cesium at room temperature for 64 hours caused the response to shift to curve 24 in Fig. 5.

During the preparation of cathodes in this laboratory it has been observed that the photoemission characteristics are to a large extent dependent upon the chemical composition of the cathode. The comparison of the 150°C to the 190°C fabrication temperature data clearly demonstrated that at 150°C a process becomes very slow which at 190° quickly destroys the photosurface for Cs/O less than 1.5. It has also been observed that after a "stable" surface is equilibrated at high temperatures its characteristics may be readily modified only by changing the composition. The composition may be changed as a result of adding more cesium or baking at a temperature higher than the equilibrating temperature. Cathodes which, after fabrication, exhibit a marked variation in spectral response characteristics depending upon the position of cathode illuminated may be made uniform in photo response characteristics by a baking operation at an appropriate temperature. After the equilibration further baking produces consistent changes independent of position on cathode. It is also true that the characteristics of a cathode with attached cesium source are invariant after a stabilizing bake provided that no significant amounts of cesium are added from the side tube.

At the end of section 1.21 the question was raised as to whether on adding cesium to a photocathode beyond Cs/O = 2 the photosensitivity could be recovered by prolonged baking at a high temperature. As the result of the experiments described in this section it is now clear that the photosensitivity can be recovered by such heat treatment, out to

cesium-oxygen ratios of almost 3. If all of the cesium added to the tube actually collected on the cathode itself and remained there, this would establish that Cs_3O is an infrared emitter which had to be activated by prolonged heating. This, however, cannot yet be accepted as a fact because it is known from the radio tracer work (Section 2) that considerable quantities of cesium accumulate on the tube envelope rather than on the cathode. The baking operations may therefore serve mainly to remove cesium from the cathode because of reaction with the tube envelope. This can be tested by adding cesium in excess, baking to restore the infrared sensitivity, and determining the amount of cesium on the cathode itself. This can readily be done by means of the radio tracer technique described in Section 2 and is planned for the immediate future.

1.23 Effect of adding excess cesium at low temperature

From the experimental data it is clear that the spectral response is a function of chemical composition and equilibration of the tube. Since at room temperature the rates of the chemical reactions at the photosurface would be slow, two experiments were performed on the effect of room temperature cesium addition on the photoemission.

After the initial fabrication of PT 53 the spectral response was measured and the cesium source was cooled overnight with a dry ice - acetone mixture. When the spectral response was remeasured the next morning, it was found to be unchanged. Thus merely standing without cesium addition has no effect on the photocathode. The cesium source was then warmed to room temperature and the change in spectral response

with time determined. The room-temperature cesium flow rate was 9.4×10^{-10} mole per hour. The change in the spectral response during 85.75 hours of cesium addition is shown by curves 2 through 7 in Fig. 6. After the response had decayed to curve 7, the tube was rebaked at 190°C with the cesium source cool to give the final response curve 8. The thermionic emission during the 190°C bake increased to a stable maximum value.

After Bake 3 cesium was again added to the tube (PT 53) at room temperature. During this cesium addition the spectral response characteristics of the tube changed from curve 11 to 16 in Fig. 7. The tube was then rebaked to constant thermionic and photoelectric emission at 150°C (Bake 4) and the spectral response 17 Fig. 7 was obtained. Rebaking the cathode thus resulted in a recovery of the original spectral response characteristics.

The change in the photoemission at 900 and 1000 mμ during the cesium addition at room temperature as a function of the amount of cesium added is shown in Fig. 8. It is evident that the photoemission at these wavelengths has decreased to a small value before the equivalent of a cesium monolayer over the entire interior surface of the tube has been added. The assumption that appreciable cesium is deposited on the walls is indicated by the following observations during the rebaking of PT 53. If the tube was rebaked after only a short period of room temperature cesium addition, then during the heating to the bake temperature the photoemission decreases gradually to the high temperature value and the thermionic emission increases continuously to the high temperature value.

Fig. 6 PT53 First room temperature
cesium addition.

Spectral Response Stage

Stage	After Warming & Source to room temperature
2	2:40 hrs. later
3	42:05 "
4	59:00 "
5	64:15 "
6	85:45 "
7	After Bake 1, 190°C
8	With Cs Source Cool

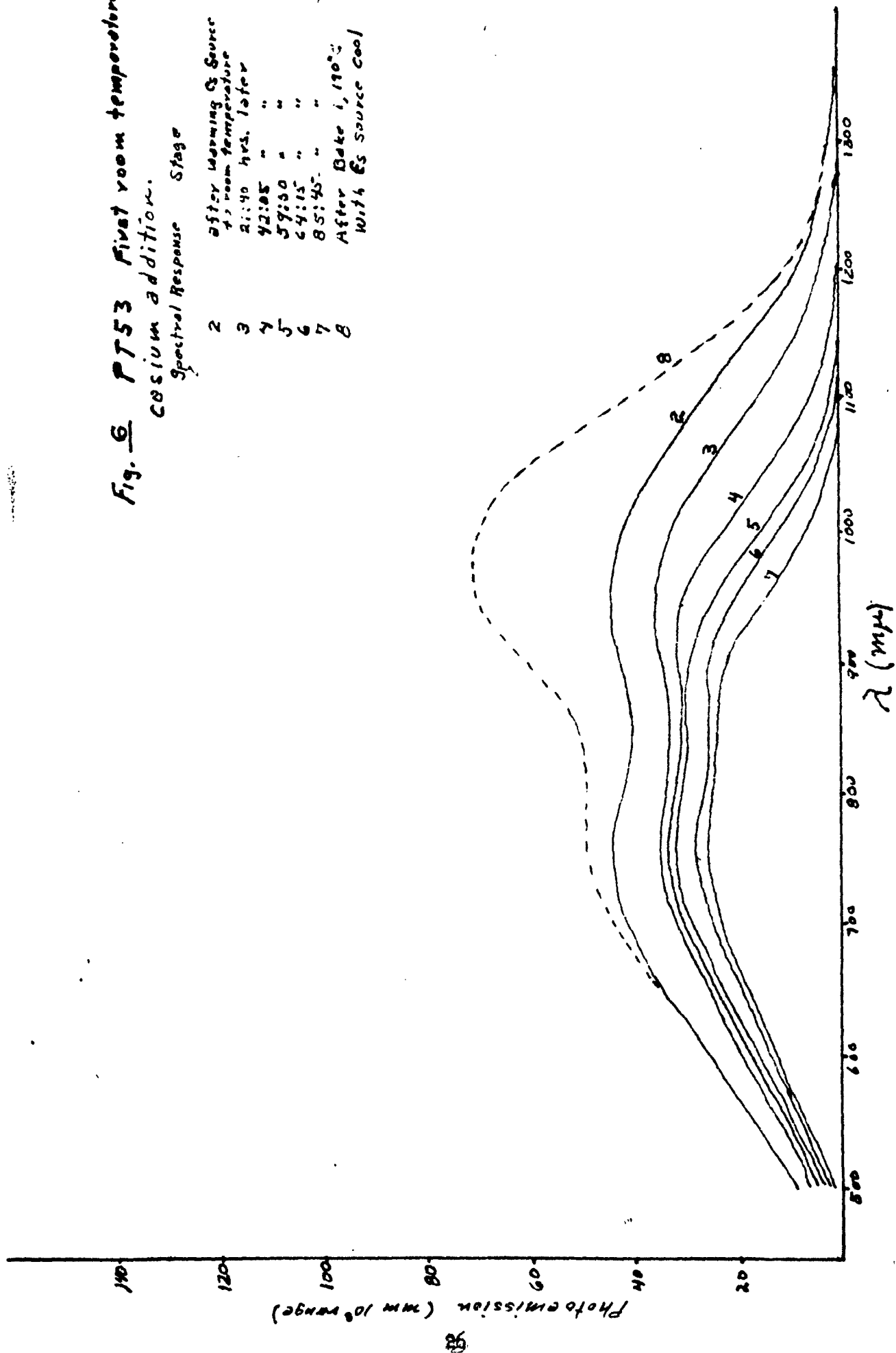


Fig. 7 PT 53 - Second room temperature cesium addition

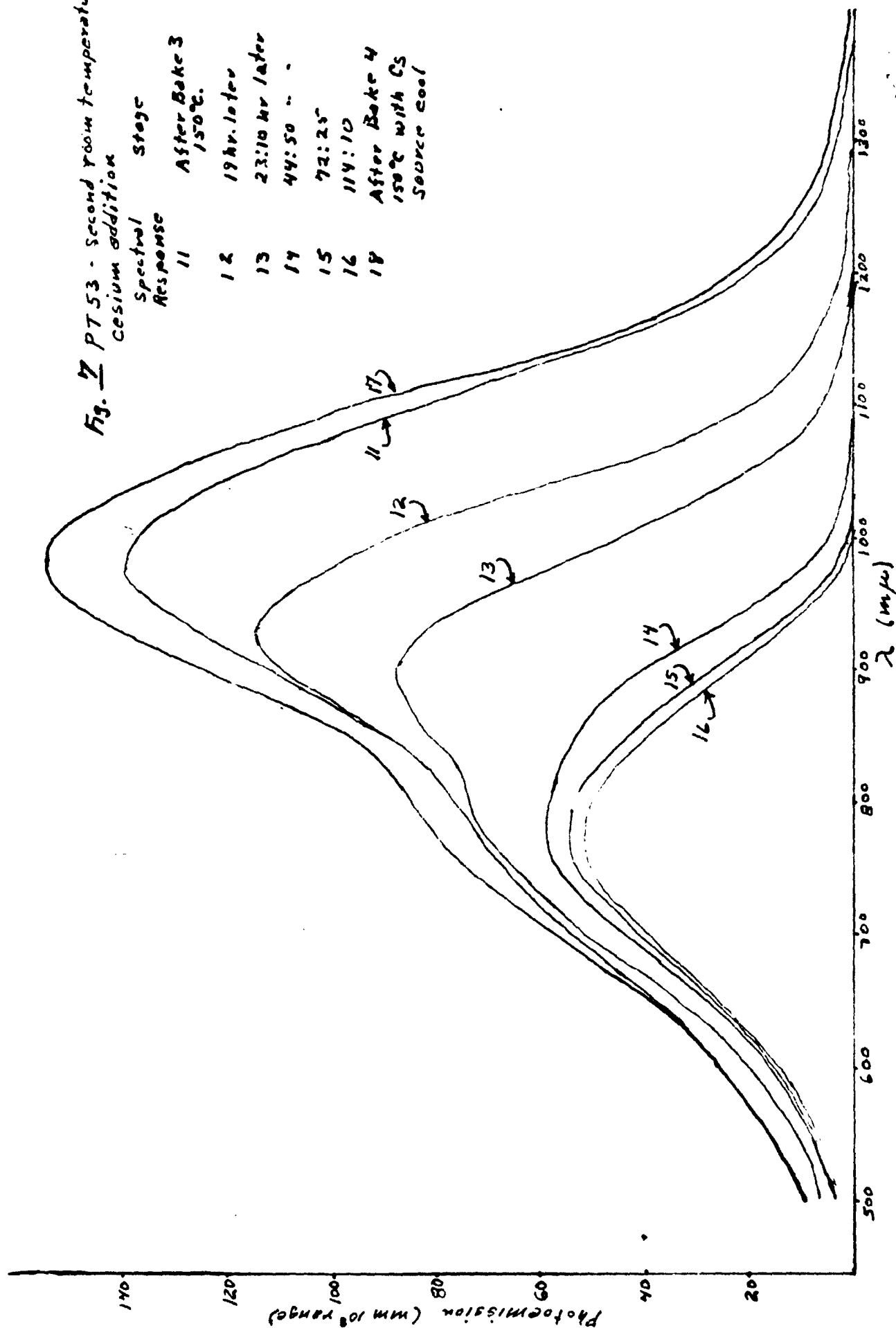


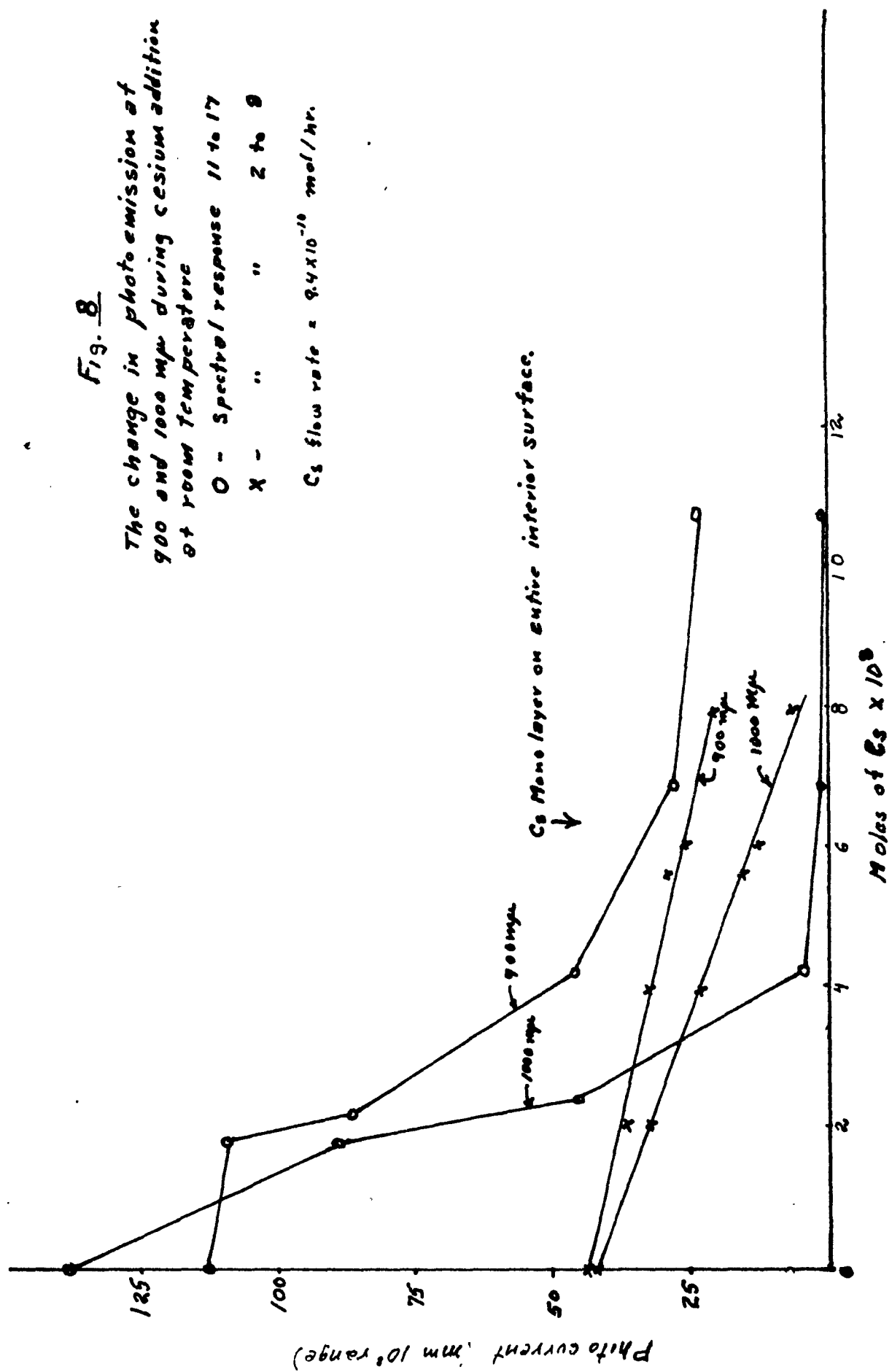
Fig. 8

The change in photoemission of
900 and 1000 mμ during cesium addition
at room temperature

O - Spectro/ response 11 to 17

X - " " 2 to 9

Cs flow rate = 9.4×10^{-10} mol/hr.



However, if significant cesium flow has occurred ($\sim 10^{-8}$ mole), then on heating the tube there is initially a rapid decrease in photoelectric and thermionic emission, followed by an increase to the former high temperature values. The decrease in emission may be interpreted as resulting from the transfer of cesium from the tube walls to the cooler cathode followed by reaction when the cathode reaches a temperature at which the reaction rates are sufficiently rapid to equilibrate the tube. The foregoing experiments explain some peculiarities encountered in the fabrication of phototubes which it seems worthwhile to describe. In the preparation of cathodes it is frequently observed that the cathode after cooling to room temperature and sealing-off from the vacuum line has a rather poor infrared response. However, after a stabilizing bake at 130°C it may develop a good set of response characteristics. Actually it has been observed that during the stabilizing bake the response may shift from the equivalent of curve 16 Fig. 8 to any of the other curves 11 through 15. After approximately a 3-hour bake at 130°C , further baking resulted only in very minor changes in the response. This behavior is probably explained by the fact that some cesium is distilled from the tube envelope to the cathode during the process of sealing-off from the vacuum line. Furthermore cathodes which after fabrication are characterized by maxima at wavelengths shorter than approximately $700\text{ m}\mu$ may not be readily baked to produce tubes with a significant response at $950\text{ m}\mu$. In this case the lack of infrared response is not due to excess cesium but to some other factor.

The data quoted above are consistent with the conclusion that the spectral response characteristics are inherently associated with the

gross chemical composition of the tube. If the cathodes are fabricated by a process such that excess cesium is present on the final room temperature photosurface, then baking will modify the response depending upon the cesium sinks present within the tube. As a result of differing processing conditions, the cesium sinks may assume varied forms. Examples of possible cesium sinks are as follows: (1) unreacted cesium oxides Cs_2O_3 , CsO_2 in the photosurface, (2) conversion of Cs_2O to Cs_3O , (3) adsorption on tube elements, and (4) reaction of cesium with the glass envelope. In a particular case, the reactions involved in the recovery of emission on baking would be dependent upon the actual gross composition of the tube and the temperature of the heat-treatment operation.

2. RADIOACTIVE TRACER EXPERIMENTS

In the previous discussion the relationship between the gross composition of the tube and the photoelectric and thermionic emission was emphasized. The composition of the cathode has been investigated using radioactive cesium to provide a means for determining the actual gross composition of the photosurface. These experiments have demonstrated that the Cs/O composition of a good cathode prepared at 190°C may vary from 0.80 to 1.49. It has also been shown that excess cesium introduction at 190°C results in a decrease in this ratio rather than an increase corresponding to a transport of oxygen away from the photosurface.

2.1 Experimental Methods

The microscope cover glass with an evaporated silver-film tube design has been adopted as standard for the radioactive cesium tracer composition determination. For the cathode, a circular silver-film of definite area with a small tongue extending to the edge is evaporated on a 0.75-inch diameter microscope cover glass. This cover glass, backed by a second blank cover glass, is mounted in a tantalum clip which makes electrical contact with the surface through the evaporated silver tongue. The second cover glass is used to eliminate the reaction of cesium with the back surface of the silvered disc. The assembled tube is similar in design to the tubes described in the previous section. The capillary for controlling the cesium flow rate during fabrication is chosen so that with the amount of oxygen deposited the tube fabrication may be completed in approximately four hours. The procedure for the preparation of the photosurface is very similar to that described in the previous section. After the completion of the cesium addition operation, the cesium source is sealed off and the tube is rebaked to establish equilibrium and to demonstrate that a "stable" photosurface has been formed. After determining the final spectral response the tube envelope is broken and the amount of cesium on the cathode and the backing disc determined, using a Geiger counter. The Cs/O mole ratio is then computed using the amount of oxygen deposited during the oxidation step.

2.2 Results

During the early stages of the investigation considerable difficulty was encountered in the preparation of a surface having good

infrared response. The cathodes were characterized by the absence of significant thermionic emission during cesium addition. Cooling the cesium source resulted in an immediate decrease in the thermionic and photoelectric emission. In addition, baking the tubes after sealing off the cesium source did not result in the development of infrared sensitivity. After considerable experimental work it was established that the difficulties were inherently related to the nature of the evaporated silver film. The initial films were prepared by a rapid evaporation of the silver. It was found that, by either evaporating the silver film very slowly or by increasing the film thickness and heat treating, a silver surface was obtained which could be oxidized satisfactorily and the reaction with cesium consistently produced a surface with good infrared response. The experiments clearly showed that the structure of the silver film could exert a profound influence upon the characteristics of the final photosurface.

A series of good infrared sensitive tracer tubes have been prepared at 190°C. During the fabrication the cesium addition was discontinued shortly beyond the maximum thermionic emission. The tube was baked with the cesium source cool until the emission became stabilized and then cooled to room temperature. After measuring the spectral response the cesium source was sealed off and the tube rebaked. During the seal-off a small amount of cesium was deposited on the surface causing a slight loss in the infrared response. During the rebaking process the original spectral response was recovered. The composition as determined by count and the spectral response characteristics of the good infrared sensitive

tubes prepared at 190°C are summarized in Table IV. From these data it is evident that the surface does not correspond to an unique chemical composition. If the cathode composition represents a distribution of cesium between Cs_2O and Cs_2O_3 , then the mole fraction of Cs_2O associated with these surfaces ranges from 0.25 to 0.83.

TABLE IV. RADIOACTIVE CESIUM
TRACER TUBES (190°C)

	Ag Film Thickness A	Cs/O Count	Wavelength (μ)		
			Peak	Longwave Limit	0.5 Maximum Current
659-28	10,000	1.01	915	~1375	1010
1588-122	20,000	1.49	950	~1375	1060
1588-130	47,000	0.80	930	1300	1030
1588-137	6,000*	1.23	930	1300	1040

* Slow Ag evaporation

During the course of the experiments, studies were made of the effect of adding cesium beyond the maximum thermionic emission. It was consistently found that the introduction of excess cesium resulted in a decrease in the cathode Cs/O mole ratio. In the experimental tubes the total surface area was large compared to the cathode area, and consequently the Cs/O ratio calculated from the cesium flow rate was consistently greater than that derived from the count because considerable quantities of cesium react with the walls of the tube. Since the variation in tube geometry from tube to tube was small, it was possible to relate the (Cs/O) by count to the (Cs/O) by flow. These data, shown in Fig. 9, indicated that the Cs/O ratio by count passes through a maximum as a function of the amount of cesium added. The results could

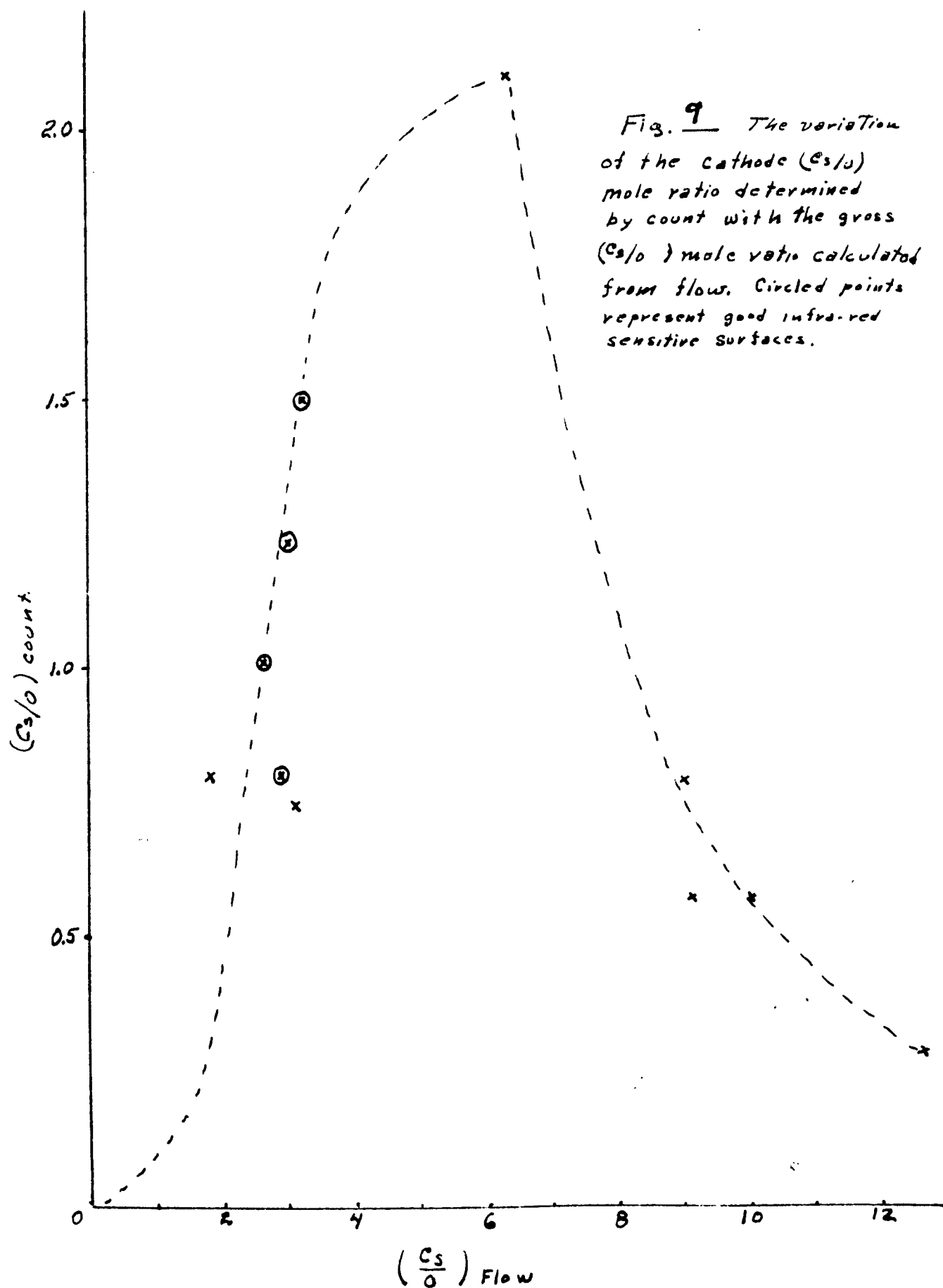


Fig. 9 The variation of the cathode (Cs/O) mole ratio determined by count with the gross (Cs/O) mole ratio calculated from flow. Circled points represent good infra-red sensitive surfaces.

not be interpreted except by the assumption that when the surface is exposed to cesium in excess of $Cs/O = 2$ at $190^{\circ}C$ there is a transport of oxygen away from the photosurface.

In the investigation of the cesium vapor pressure of the surface at $145^{\circ}C$ Sayama⁽²⁾ found that when the gross composition approached Cs_3O , the ionization gauge characteristics as a function of the filament temperature were no longer typical of cesium. He suggests that this behavior can be explained if the observed vapor pressure is due to molecules of a cesium suboxide such as Cs_3O which has an ionization potential greater than the electron affinity of tungsten. Formation of a volatile oxide would account for the transport of oxygen from the cathode, as suggested by the above radio-tracer experiments. This phenomenon is unquestionably important in the fabrication of photocathodes.

It is finally of some interest that radioactive cesium is invariably found on the glass after fabrication of a phototube. This is established by measuring the activity of the microscope cover glass which is placed on the back of the glass disc on which the cathode is prepared. If the activity per unit area of this glass backing disc is assumed to apply to the whole tube envelope, then for photocathodes such as those of Table IV the amount of cesium on the tube walls is nearly the same as that on the cathode. It is strongly suggested that this cesium reacts chemically with the glass.

3. CRYSTAL STRUCTURE OF Cs_2O

The study of the crystal structure of Cs_2O is being continued in order to further refine the parameters. Absorption corrections have been

calculated on two sets of single crystal reflections, one obtained with CuK_α and the other with MoK_α x-radiation. Structure factors have been calculated from the corrected intensity data and are in quite satisfactory agreement. Calculations of electron density are under way. Both line sections and projections are being calculated. These calculations are continuing.

NOTE: In submitting this report it is understood that all provisions of the contract between The Foundation and the Cooperator and pertaining to publicity of subject matter will be rigidly observed.

Investigator Date

Supervisor Edwin M. Lassiter Date Aug. 18, 1953

For The Ohio State University Research Foundation

Executive Director Oran C. Woodbert Date 8/19/53